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Microphase separation in hydrogen bonding polymer/surfactant melts

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Abstract

Phase behavior of solvent free mixtures of homopolymers and amphiphiles capable of hydrogen bonding is analyzed in weak segregation limit applying a theoretical model describing the main features of the system as a function of composition, temperature and strength of hydrogen bonding. Phase diagrams obtained contain relatively small regions of stable ordered structures, while the regions of macrophase separation representing equilibria between ordered and homogeneous phases are rather broad. The influence of the surfactant (amphiphile) length on the order–disorder transition temperature and the critical wave vector is studied. The phenomenon of reappearing homogeneous phase is considered. The predictions of the present theory for experimental systems are thoroughly discussed on the basis of a comparison with the extensively investigated poly(4-vinyl pyridine)–amphiphile systems taking into account the limitations of the model applied.

Keywords: Microphage separation; Phase diagram; Hydrogen bonds; Polymer–amphiphile mixtures

1. Introduction

Microphase separation is a widespread phenomenon in polymer systems including various polymer/surfactant systems involving charged, as well as uncharged, surfactants [1–17]. The investigation of comb copolymer-like systems involving hydrogen bonding started only very recently [4,8,9,13,16]. These systems are of considerable interest, because they demonstrate a wide variety of self-organizing properties, which can often be controlled in a simple way by changing the external parameters.

The present paper is devoted to analytical considerations of the phase behaviour in hydrogen bonding polymer/surfactant mixtures in relation to experimental results. In these kind of systems both macro- and microphase separation can be expected (Fig. 1). Indeed, as a normal two-component mixture the polymer system under consideration tends to segregate at low temperatures due to component incompatibility (Fig. 1a). In this case a polymer-rich and a surfactant-rich phase would coexist on a macroscopic level. On the other hand, a polymer chain hydrogen bonded with surfactants represents a comb copolymer-like molecule. At low temperatures and high degrees of complexation the system is in fact a mixture of

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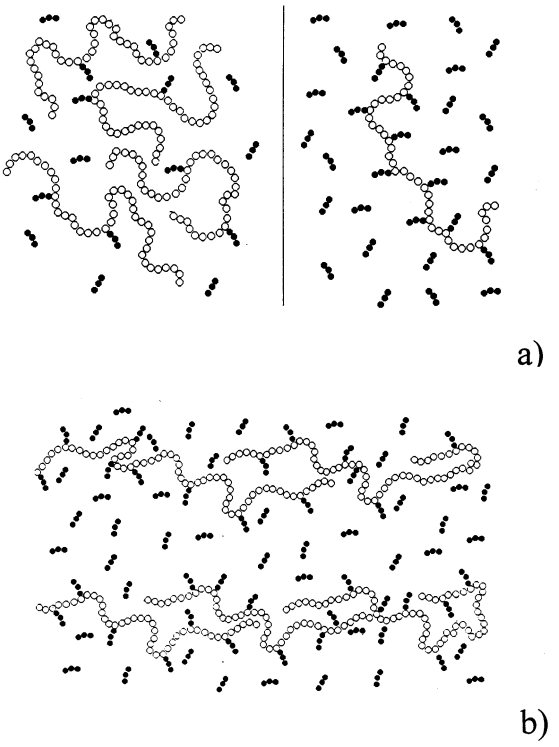

Fig. 1. Schematic picture of macrophase (a) and microphase (b) (lamellar structure) separation for hydrogen bonding polymer/surfactant melt.

comb copolymer-like molecules, which are nearly identical, and free surfactants, the latter in amounts depending on the composition. For stoichiometric composition full complexation is possible. In this case there are no free surfactants and only comb copolymer-like molecules are present. Due to the segregation tendency between polymers and 'side-chain' surfactants, microphase separation similar to that in the conventional chemically bonded comb copolymers [18–21] can occur (Fig. 1b). However, the polymer system under consideration essentially differs from the latter, since hydrogen bonding is a temperature (and composition) dependent process. As a result, the fraction of hydrogen bonds and free surfactants changes with temperature. Another important feature of the polymer system is the reversibility of hydrogen bonds in contrast to chemical ones. Because of this, the polymer system under consideration promises a much more rich phase behaviour than chemically bonded comb copolymers.

Phase separation was recently studied analytically for systems of associating polymers by Tanaka [22]. The average degree of association was obtained by a multistage calculation involving the consideration of intermediate clusters. Spinodal curves for both macro- and microphase separation were derived using the random phase approximation (RPA) approach. The phase diagrams were, however, calculated assuming that the free energy of the ordered state is the same as for the homogeneous state.

In the present paper we present the results of a slightly different approach, discussed in detail in Ref. [23]. The average fraction of hydrogen bonds per chain is calculated directly by minimization of the free energy of the homogeneous state. As a result, the expression for the average number of hydrogen bonds per chain is different from that obtained by Tanaka [22]. Our phase diagrams are obtained by solving the equations of phase equilibria for different coexistent phases. The free energy of the ordered structures is calculated via the standard RPA approach which involves the considerations of higher order correlation functions [24].

The theoretical predictions will be compared in detail with the available experimental data [8–11,13–16] involving poly(4-vinyl pyridine) (P4VP) as a prototype hydrogen bond accepting polymer. (P4VP)/pentadecylphenol (PDP) mixtures have been studied by small-angle (SAXS) and wide-angle (WAXS) X-ray scattering, as well as by differential scanning calorimetry and dynamic mechanical analysis [8,11,13,14]. A pronounced order–disorder transition has been observed for various compositions of P4VP-PDP$_X$, where X represents the ratio between the number of phenol and pyridine groups. In all cases the ordered structures observed correspond, according to the SAXS data, to a lamellar morphology. Very recently the same system with a somewhat longer alkyl tail, i.e. *p*-nonadecylphenol, was studied by transmission electron microscopy and the first pictures of the highly ordered lamellar structures were obtained [17]. The polymer system has also

been modified in a different way by introducing sulphonic acids, such as methyl sulphonic acid (MSA) as a quaternization agent [16]. The quaternization results in poly(4-vinyl pyridinium methyl sulphonate), and the sulphonate groups in turn act as hydrogen bonding acceptors for the alkyl phenols. P4VP-$MSA_{1.0}$-$PDP_{1.0}$ mixtures have been studied by SAXS and optical microscopy [16]. The order–disorder transition to a lamellar structure also occurs in this system but now at around 100°C instead of the 60°C for the system without MSA. Moreover, the phase behaviour turned out to be considerably more complex, including the phenomenon of reappearing phases.

2. Model

Let us consider a solvent-free polymer/surfactant mixture, in which hydrogen bonds can be formed between the head of the surfactant molecules and the monomer units of the polymer chains. The length of homopolymer chains is denoted by N_p and the length of the surfactants by N_s The composition of the mixture will be expressed in terms of the fraction of surfactant molecules per monomer unit of the polymer chains, X. Hence, the case $X=1$ corresponds to the stoichiometric composition.

As is well known, the strength of hydrogen bonding (hb) can be different depending on the molecules involved in the hb formation. The strength of the hydrogen bonds can be expressed in terms of the equilibrium constant of the reaction K

$$\Phi_{hb} = K\Phi_m\Phi_{fs} \tag{1}$$

where Φ_{hb} is the volume fraction of surfactants hydrogen bonded with polymer chains, Φ_m and Φ_{fs} are the volume fractions of 'free' monomer units of the polymer chains and free surfactants, respectively.

Hydrogen bond formation is temperature dependent. As a result, the equilibrium constant K is a function of temperature. Two different contributions—temperature dependent and temperature independent—, can be distinguished:

$$K = \exp\left(\frac{E}{T} - S\right) \tag{2}$$

The coefficient E of the temperature dependent term, characterizes in fact the energetic gain (in comparison with kT) due to the formation of one hydrogen bond.

The energetic gain is large especially for low temperatures, where hydrogen bonding will happen easily.

The other coefficient, S, can be considered as the entropy loss due to the formation of one hydrogen bond. Hydrogen bonding is very directionally specific and to form a hydrogen bond, a surfactant molecule should have the 'correct' orientation with respect to the corresponding monomer unit of the polymer chain [25]. Thus, the interplay between energetic gain and entropic loss determines the formation of hydrogen bonds in the system.

The available experimental data indicate that hydrogen bonding, at least for most of the systems considered so far, seems to be non-cooperative. In other words, hydrogen bonds can be formed (broken) at any 'point' of a polymer chain independently of the presence (absence) of other hydrogen bonds in the surrounding. Due to this, the probability P to find a polymer chain with a fixed number of hb, n, satisfies the binomial law. The exact form of the distribution can be obtained by the minimization of the free energy of the homogeneous state of the system [23]:

$$P_n = C_n^{N_p}\left(\frac{\langle n\rangle}{N_p}\right)^n\left(1-\frac{\langle n\rangle}{N_p}\right)^{N_p-n}, \tag{3}$$

where

$$C_n^{N_p} = \frac{N_p!}{n!(N_p-n)!}$$

is the coefficient of the binomial distribution.

The average fraction of hb per chain $X_{hb} \equiv \langle n\rangle/N_p$ is a function of temperature, composition and strength of hydrogen bonding [23]:

$$X_{hb} = \tfrac{1}{2}\{A - \sqrt{A^2-4X}\} \tag{4}$$

$$A = 1 + X + (1 + XN_s)/K \equiv$$

$$\equiv 1 + X + (1 + XN_s)\exp\left(S - \frac{E}{T}\right)$$

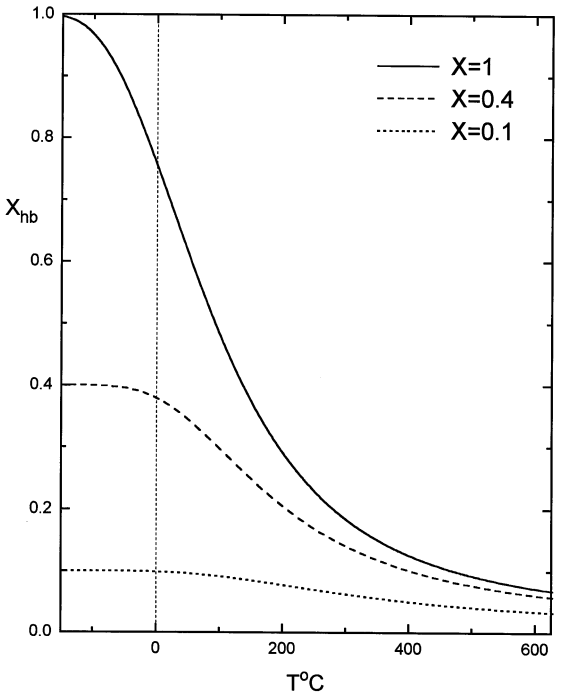

Fig. 2. Temperature dependence of the average fraction of hydrogen bonds per chain X_{hb} for the polymer systems ($N_p = 10^3$, $N_s = 15$, $E = 2000$ K, $S = 2$, $\Theta = 155$ K) with different average fraction of surfactants X.

A typical temperature dependence of the average degree of complexation, X_{hb}, is presented in Fig. 2. As can be seen from it, the average fraction of hb increases substantially as the temperature decreases. In the limit of low temperatures, where hydrogen bonding is preferable, X_{hb} tends to the average fraction of surfactants per monomer unit of polymer chains, X, for $X < 1$ (polymer excess), or it tends to unityfor $X \geq 1$ (surfactant excess). It means that in this temperature region either all surfactants are hydrogen bonded with the polymer chains ($X < 1$) or all the monomer units of the polymer chains are occupied by surfactants ($X \geq 1$) and additionally free surfactant molecules remain in the system. The boundary case $X = 1$ corresponds to stoichiometric composition. In this case full complexation is possible for low temperatures, when all surfactants and all monomer units of the polymer chains take part in hb formation.

The average degree of complexation, X_{hb}, depends also on the strength of hydrogen bonding, i.e. on the equilibrium constant K (Fig. 3). An increase of E (energetic gain) or decrease of S (entropy loss) results in an increase of the average fraction of hydrogen bonds per chain X_{hb}. It is worthwhile to note that not only the absolute value of X_{hb}, but also the 'abruptness' of its temperature dependence is an important feature of the system. The stronger the hydrogen bonding (larger E and smaller S) the more smooth the temperature dependence.

It is important to emphasize already here that the temperature dependences of X_{hb} considered above correspond to the homogeneous state of the system. Macrophase separation can substantially influence hb formation ([23]).

A theoretical approach for studying the phase behavior of these polymer systems was introduced and discussed in Ref. [23]. It is based on using the random phase approximation (RPA) method (i.e.

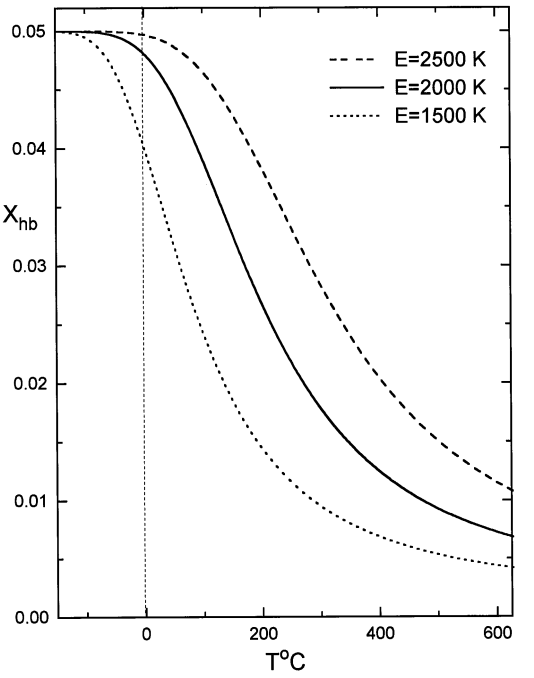

Fig. 3. Temperature dependence of the average fraction of hydrogen bonds per chain X_{hb} for the polymer systems ($N_p = 10^3$, $N_s = 15$, $S = 3.5$, $\Theta = 155$ K, $X = 0.05$) with different strength of hydrogen bonding.

weak segregation limit). In frameworks of RPA, the free energy expansion into a power series of the fluctuating parameter (such as the polymer volume fraction) is analyzed. The results obtained in RPA approach are valid for weak fluctuations, i.e. as long as the polymer system is not far from the spinodal of microphase separation. Here we will discuss only those results of the theoretical model [23] which can be compared with the experimental data.

The polymer system under investigation can in fact be considered as a mixture of random comb copolymer chains (subjected to the binomial distribution (Eq. (3))) and free surfactants. Using this analogy between the present polymer system and conventional block copolymers, the correlation functions providing the information about the behaviour of the system can be calculated [18–21,23,24]. The specific feature of the system under consideration is the temperature dependence of the fraction of 'side chains' (hydrogen bonded surfactants) and free surfactants. As a result, the polymer surfactant and surfactant–surfactant correlation functions become temperature dependent through the average values

$$\langle n \rangle = N_p X_{hb}$$

and

$$\langle n(n-1) \rangle = N_p^2 X_{hb}^2 \left(1 - \frac{1}{N_p}\right),$$

respectively [23].

On the base of the second order correlation functions S_{ij} ($i = p$, for polymer units, $i = s$, for surfactant units), the structure factor $S(q)$ can be obtained

$$S(q) = \frac{1}{S^0(q) - \frac{\Theta}{T}} \tag{5}$$

$$S^0(q) = \frac{S_{pp} + S_{ss} + 2S_{ps}}{S_{pp}S_{ss} - S_{ps}^2}, \tag{6}$$

where Θ is the Θ-temperature for polymer/surfactant monomers melt. Θ-temperature is connected with χ-parameter of the polymer–surfactant interactions via the relation $\chi = \Theta/2T$.

The regions of instability with respect to microphase ($q^* \neq 0$) and macrophase ($q^* = 0$) separation (i.e. spinodal curves) can be defined by the set of equations

$$\begin{cases} \dfrac{\partial S^0(q)}{\partial q}\Big|_{q=q^*} = 0 \\ S^0(q^*) - \theta/T = 0 \end{cases} \tag{7}$$

Spinodal for macrophase separation can be obtained from the Eq. (7) as well as it can be calculated starting from the free energy of homogeneous state:

$$\frac{\Theta}{T^{mac}} = \frac{XN_s + 1}{N_p} + \frac{(1 + X_{hb}N_s)^2}{N_s\left(1 - \dfrac{1 + N_s X_{hb}^2}{1 + N_s X}\right)}. \tag{8}$$

Spinodal for microphase separation and critical wave vector has been obtained from numerical solution of Eq. (7). In the limit $(q^2a^2N_s/6) \gg 1$ the value of critical wave vector can be estimated as

$$\frac{q^{*2}a^2}{6} \sim \sqrt{\frac{X_{hb}}{1 + XN_s}\left(\frac{1}{N_s} + X_{hb}\left(1 - \frac{1}{N_p}\right)\right) - \frac{1}{4(1 + XN_s)}\left(\frac{1}{N_p^2} - \frac{1}{N_s^2}\right) - \frac{1}{4N_s^2}} \tag{9}$$

The dependence of critical wave vector q^* on the composition is rather complicated taking into account that X_{hb} is also composition dependent (Eq. (4)).

The structure factor $S(q)$ tends to zero in the limit of large q like $1/q^2$

$$S(q) \sim 12\ \frac{XN_s}{(1 + XN_s)^2}\ \frac{1}{q^2a^2}. \tag{10}$$

In the limit of small

$$qu\left(\frac{q^2a^2N_p}{6} \ll 1\right)$$

the structure factor $S(q)$ depends on q like

$$S(q) \sim \frac{1}{\dfrac{\Theta}{T^{mac}} - \dfrac{\Theta}{T}} + f(X)q^2 \tag{11}$$

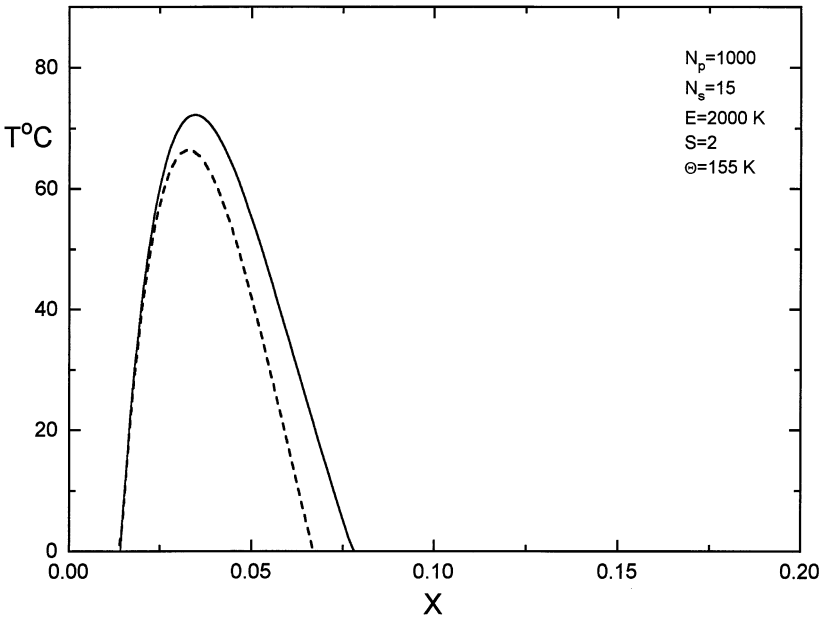

Fig. 4. Spinodal curves for macro- (dashed curve) and microphase (solid curve) separation for systems with strong hydrogen bonding ($N_p = 10^3$, $N_s = 15$, $E = 2000$ K, $S = 2$, $\Theta = 155$ K).

where T^{mac} is the temperature corresponding to spinodal of macrophase separation (Eq. (8)), $f(X)$ is complex function of composition, chain lengths, temperature and strength of hb.

Spinodal curves for microphase (solid curve) and macrophase separation (dashed curve) are presented in Fig. 4 for a polymer/surfactant system with strong hydrogen bonding. As can be seen from this figure, a pronounced increase of instability of the homogeneous state (as the temperature decreases) can be expected for polymer systems with a small number of surfactant molecules compared to stoichiometric conditions (i.e. $X \ll 1$). But do note, that the top of the spinodal occurs for nearly equal volume fractions of both components. As discussed above, for such polymer systems the average fraction of hydrogen bonds X_{hb} is small even in the low temperatures region where almost all surfactants take part in hydrogen bond formation. The system represents a mixture of comb copolymer-like chains with different number of side-chains (hydrogen bonded surfactant molecules). A segregation tendency between polymer and surfactant components can therefore be resolved by both micro- and macrophase separation. In polymer systems with larger amounts of surfactants the situation is different. Due to a larger degree of complexation, X_{hb}, the comb copolymer-like molecules become more and more identical and at the same time also more compatible with a solvent of free surfactants. In general, this will prevent macrophase separation into homogeneous phases.

To obtain the phase diagram for the polymer system under consideration the free energies for the different ordered structures have to be studied. The standard RPA technique is applied for calculation of the free energy for ordered phases (BCC, hexagonal, lamellar) [24]

$$\frac{F_n}{kT} = \frac{F_0}{kT} + \left(\frac{\theta}{T^*} - \frac{\theta}{T}\right)\Psi_i^2 - \alpha_i\Psi_i^3 + \beta_i\Psi_i^4 \qquad (12)$$

where F_0 is the free energy of the homogeneous state, Ψ_n is the amplitude of an ordered phase and the coefficients α_i, β_i are connected with the higher order correlation functions (through the coefficients Γ_3, Γ_4) depending on the symmetry of the ordered structure ($i = 1$ corresponds to lamellar, $i = 3$ to hexagonal and $i = 6$ to BCC structures) [24] $\alpha_1 = 0$, $\beta_1 = \Gamma_4(0, 0)/4$; $\alpha_3 = (-2/3\sqrt{3})\ \Gamma_3$,

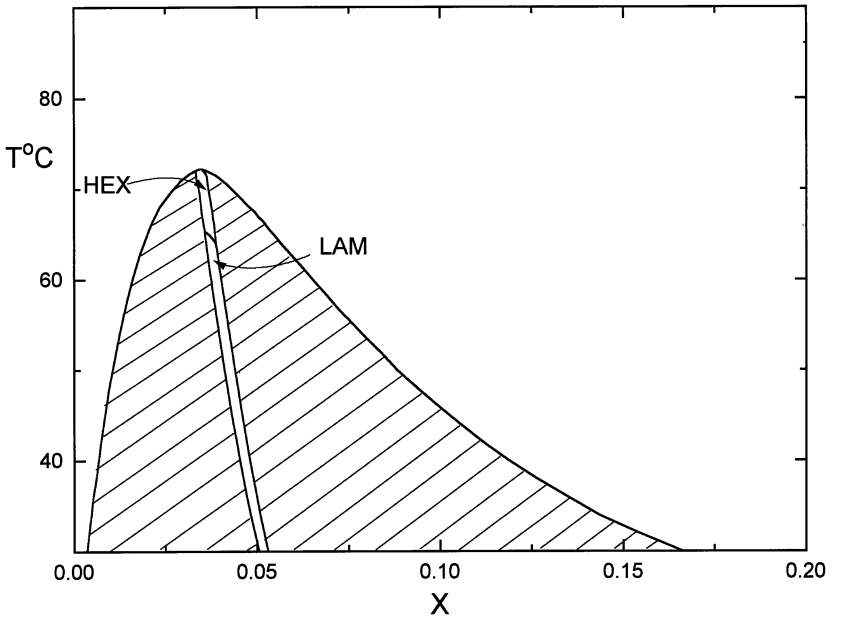

Fig. 5. Phase diagram for polymer–surfactant mixture with strong hydrogen bonding ($N_p = 10^3$, $N_s = 15$, $E = 2000$ K, $S = 2$, $\Theta = 155$ K). Diagram contains regions of stability of the hexagonal (HEX) and the lamellar (LAM) ordered phases as well as large regions of macrophase separation (shaded areas).

$\beta_3 = (\Gamma_4(0, 0) + 4\Gamma_4(0, 1))/12$; $\alpha_6 = (-4/3\sqrt{6})\ \Gamma_3$, $\beta_6 = (\Gamma_4(0, 0) + 8\Gamma_4(0, 1) + 2\Gamma_4(0, 2) + 4\Gamma_4(1, 2))/24$.

Comparing free energies of ordered phase and the homogeneous one it is possible to define the regions where an ordered phase has the lowest free energy. However, to analyse the equilibrium state of the system (to obtain a phase diagram) the possibility of macrophase separation into a homogeneous and an ordered phase or into two different ordered phases has to be taken into account as well. To this end the following set of equations of phase equilibrium can be solved:

$$\begin{cases} \dfrac{dF_i}{d\Phi}\Big|_{\Phi=\Phi_1} = \dfrac{dF_j}{d\Phi}\Big|_{\Phi=\Phi_2} \\ \left\{\Phi\dfrac{dF_i}{d\Phi} - F_i\right\}\Big|_{\Phi=\Phi_1} = \left\{\Phi\dfrac{dF_j}{d\Phi} - F_j\right\}\Big|_{\Phi=\Phi_2} \end{cases} \quad (13)$$

The first equation corresponds to the condition of equality of 'chemical potentials' of the coexistent phases. The second equation results from the condition of equality of osmotic pressures of the phases. The 'chemical' potentials and pressures of the phases has been calculated based on the expressions for the free energies (Eq. (12)).

Since the details of the calculations are presented elsewhere [23], we will discuss only the main results in comparison with the experimental observations.

3. Results and discussion

3.1. Phase diagram for polymer/surfactant melt with strong hydrogen bonding

A typical phase diagram for a polymer system with strong hydrogen bonding is presented in Fig. 5, corresponding to the same system for which the spinodal curves are plotted in Fig. 4. As is seen from the diagram, the regions of macrophase separation into a homogeneous and an ordered phase occupy a large part of the diagram. The small regions of stable ordered structures are located near the 'critical point' of the diagram, in the region of comparable volume fraction surfac-

tants and polymers. This region corresponds to values of X smaller than that for the stoichiometric condition. It is not a surprise that the polymer/surfactant mixture becomes incompatible (as temperature decreases) firstly in the region with polymer excess. In this region the degree of association (Eq. (4)) is lower than in the regions with larger X (Fig. 2), which promotes the instability with respect to both macro- and microphase separation. Due to this, stable ordered phase arises for polymer/surfactant mixture with small X at higher temperature than that for mixtures with $X=1$ or higher X. The higher X the larger degree of association and hence the longer the homogeneous state remains stable with a decrease of the temperature. The regions of stable ordered phases (hexagonal and lamellar) presented in Fig. 5 are rather narrow. Of course, this does not mean, that microphase separation can be observed only in these particular temperature and composition intervals. The wide regions of macrophase coexistence makes it possible to observe ordering (at least for one of the coexistent phases) in the system for a broad composition range. Indeed, a hexagonal phase can be observed for polymer systems with a composition inside the interval $0.017 \leq X \leq 0.055$ at temperatures 65–72°C. For lower temperatures a coexistence between a lamellar and a homogeneous phase can take place for polymer systems belonging to an even broader composition range.

Now let us turn to the experimental results for P4VP-PDP. The order–disorder transition (ODT) temperature is a strong function of X. The maximum value of ODT temperature corresponds to stoichiometric compositions. In this system microphase separation into a lamellar phase is observed for $0.25 < X < 1.5$. No clear indications for macrophase separation are found yet [11,15]. However, the whole issue of macrophase separation has not been investigated systematically so far. At first sight, these results differ completely from the theoretical predictions. Closer inspection shows that this is not necessarily the case.

In the P4VP-PDP$_X$ system $X=1.0$ corresponds to equal numbers of surfactants and monomer units of polymer chains and simultaneously it corresponds to comparable volume fractions of polar (pyridine + phenol) and non-polar alkyl material [8]. This is due to the large difference in size between CH_2 units and phenol or pyridine. In the framework of the theoretical model the difference in the sizes was neglected to simplify calculations. As a result both conditions $X=1$ and equality of polymer and surfactant volume fractions are fulfilled only for the case of extremely short surfactant chains $N_s=1$, however for this case the validity of RPA approach becomes doubtful. Thus, if we take into account this difference between the theoretical model and the real experimental system, the most appropriate condition for the comparison seems to be equality of volume fractions. This implies that the experimental situation corresponds to values of X around 0.06 for the theoretical model (in the case of $N_s=15$). And this is close to the range of polymer volume fractions for which the stable ordered structures occur. Nevertheless, it is important to realize that a direct comparison is difficult and it is possible to expect that the phase behavior might change considerably, when the specific features of real polymer system are explicitly taken into account.

On the other hand there is also another intriguing possibility. Even if macrophase separation into an ordered state and a homogeneous state corresponds to the lowest free energy, it is not certain that this state will also be easily achieved experimentally. As Fig. 5 demonstrates, starting from $X=0.1$, the macrophase separation requires a redistribution of surfactants over the polymers in order to obtain equilibrium between an ordered phase with $X \simeq 0.05$ and nearly absence of free surfactants and a homogeneous phase with $X > 0.1$. This process might be very slow so that during normal time of scan measurements the real equilibrium can not be achieved and microphase separation into an ordered structure with a periodicity determined by the critical wave vector occurs.

The parameters values for the theoretical model have been chosen in such a way that no macrophase separation occurs at elevated temperatures. The number of hydrogen bonds decreases dramatically, as the temperature increases, however the repulsive interactions are already too small (compared to kT) to induce phase separation. This is exactly the situation of the P4VP-PDP system.

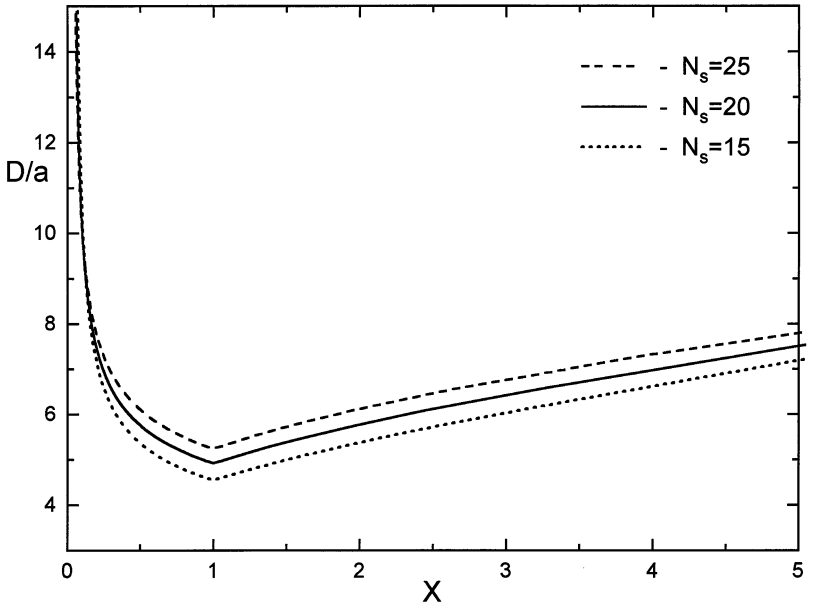

Fig. 6. The dependence of the period of ordered structures D (per monomer volume a) on the average fraction of surfactants X for the systems ($N_p = 10^3$, $E = 4000$ K, $S = 1$, $\Theta = 150$ K) with different surfactant lengths N_s.

As was discussed above, the regions of macrophase separation in the phase diagram are rather broad. In many respects it reflects the specific features of the polymer system. However, a decrease of the regions of stable ordered structures typical for, e.g. diblock copolymer melts [24,26] and an appearance of relatively large two phase regions of coexistence between homogeneous and ordered phases due to addition of homopolymer (solvent) are well known phenomena [27,28]. A direct comparison with the case of homopolymer/diblock copolymer melts is obviously impossible, due to the difference in molecular architecture and in the nature of chemical and hydrogen bonds. Indeed, even for a melt of comb copolymers, the phase diagram [20] differs from that for diblock copolymers [24,26]. The presence of free surfactants in amounts depending on temperature, composition and strength of hb makes the phase behavior more complicated, especially considering that some of the hydrogen bonds can be broken even at low temperature due to, e.g. macrophase separation [23].

It is worthwhile emphasizing that the theoretical results obtained within the framework of RPA approach are valid as long as we are not very far from the spinodal for microphase separation. Otherwise a different analysis involving the strong segregation limit is required.

3.2. Period of ordered structures

Fig. 6 presents the period of ordered structure (critical wave length $2\pi/q^*$) corresponding to the critical wave vector q^* of the spinodal for microphase separation (Fig. 7) as a function of X. $2\pi/q^*$ corresponds to the period D of the microphase structures, provided macrophase separation does not intervene. The decrease of the critical wavelength for increasing values of X (until $X = 1$) is well described by a $1/X^{\alpha}$ dependence, where α is about unity. Experimentally, the period of the lamellar structures found in P4VP-PDP$_X$ does satisfy the $1/X$ dependence [8,9]. The same functional dependence is also observed for the position of the correlation hole scattering peak in the homogeneous state. Theoretically, the minimal value of the period corresponds to $X = 1$ (Fig. 6). An increase in either of the component concentration results in an increase of the critical

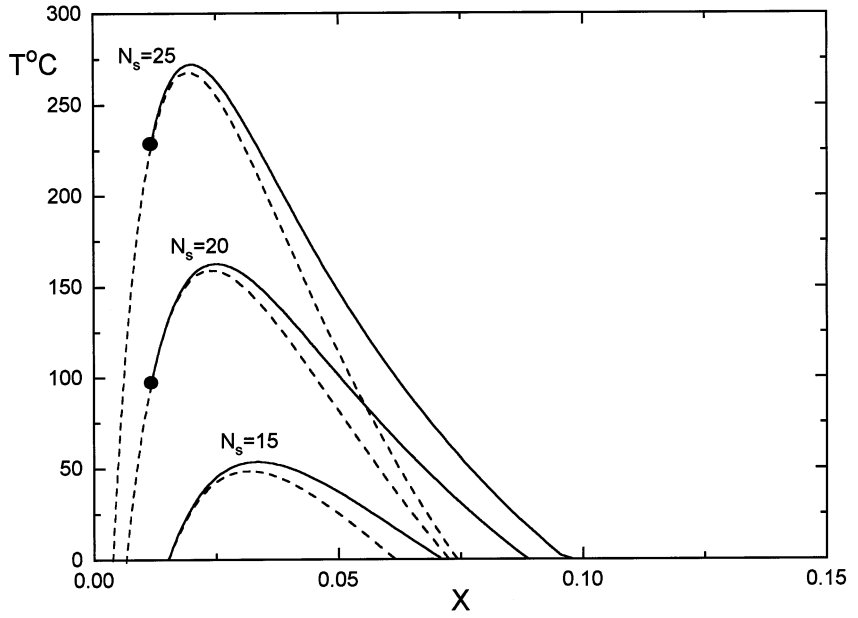

Fig. 7. Spinodal curves for microphase separation for mixtures ($N_p = 10^3$, $E = 4000$ K, $S = 1$, $\Theta = 150$ K) with different surfactant lengths. Large solid points correspond to Lifshitz points.

wavelength. This phenomenon can be easily explained by the fact that an increase (decrease) of X means an increase of surfactant (polymer) fraction in the system, which results in an expansion of the surfactant-rich (polymer-rich) regions. For extremely low (high) surfactant concentration the period tends to infinity, since this case corresponds in fact to a one-component system. It is important to realize that the value of the period of the ordered structures obtained on the basis of the critical wave vector is correct as long as the system is near the ODT, for lower temperatures considerable differences between theory and experiments are possible.

3.3. The influence of the surfactant length on the order disorder transition

Recent experimental observations demonstrate that an increase in length of the surfactant molecule results in an increase of the order–disorder transition temperature [16,17]. Indeed, for pentadecylphenol molecules (mixed with P4VP) the temperature of the order–disorder transition (ODT) is approximately 60°C for $X = 1.0$ (equal volume fractions for polar and non-polar alkyl material). For nonadecylphenol/P4VP mixture the ODT temperature increases to approximately 100°C at the same composition, i.e. at $X = 1$ (volume fraction of polar material is less than for non-polar one). The difference is similar for the range of values of X investigated.

Fig. 7 presents a set of theoretically calculated spinodal curves of microphase separation for polymer systems with different surfactant lengths. The most pronounced difference between the spinodals occurs in the composition range of low X values near equal volume fraction conditions. As can be seen from Fig. 7, in this composition range the temperature of the order–disorder transition corresponds to approximately 58°C for $N_s = 15$, whereas for $N_s = 20$ the ODT temperature increases to approximately 165°C.

The tendency for ODT temperature to increase is clearly seen from both experimental and theoretical results. To analyze the physical reason for this phenomenon let us compare polymer mixtures with the same composition X, but different surfactant length. As discussed above, the experimental data for P4VP-$PDP_{1.0}$ can be best com-

pared with theoretical results for equal volume fractions of polymer and surfactants, i.e. $X \simeq 0.06$. The increase of surfactant length results in a decrease of the polymer volume fraction (as for the case of nonadecylphenol surfactants), implying a reduction in the number of polymer chains and therefore a decrease in the number of monomer units of polymer chains available for hydrogen bonding. In this situation it is to be expected that the average fraction of hydrogen bonds per chain X_{hb} decreases as well. This effect might become especially important at elevated temperatures, where X_{hb} is strongly dependent on the probability of contacts between free surfactant and 'free' monomer units of the polymer chains. Indeed, the temperature dependences of X_{hb} for different surfactant lengths (and fixed composition X), presented in Fig. 8, confirm our expectations: the average degree of association is larger for shorter surfactant chains. This tendency can also be seen clearly from (Eq. (4)) in the limit of high temperatures

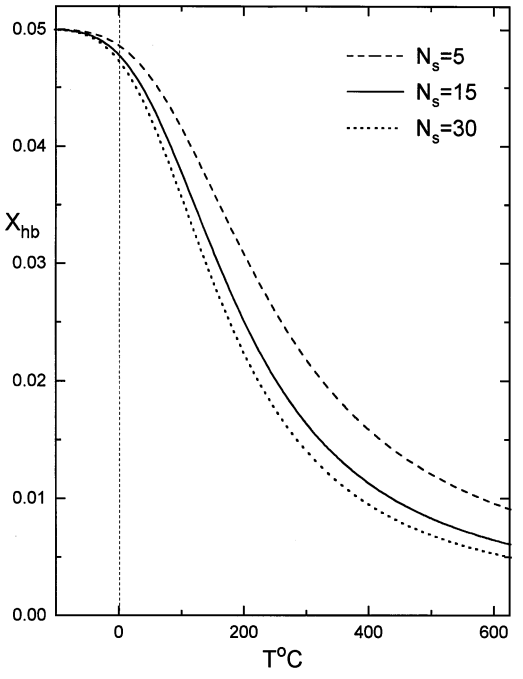

Fig. 8. Temperature dependence of the average fraction of hydrogen bonds per chain X_{hb} for the polymer systems ($N_p = 10^3$, $E = 2000$ K, $S = 3.5$, $\Theta = 155$ K, $X = 0.05$) with different surfactant lengths.

$$X_{hb|_{T\gg 1}} \sim \frac{X}{A} \equiv \frac{XK}{(1+X)K + 1 + XN_S}. \quad (14)$$

The smaller the fraction of hb per chain X_{hb}, the less stable the homogeneous state of the mixture (with respect to both microphase and macrophase separation), which results in an increase of ODT temperature for longer surfactants. This tendency for the ODT temperature to increase as a function of surfactant chain length is true not only for $X \simeq 0.06$, which corresponds to equal volume fractions of P4VP-PDP$_{1.0}$, but also for the other mixture compositions.

The period of the structure D (corresponding to the ODT temperature) also depends on the surfactant length (Fig. 6). With the exception of the regions of extremely large or small fractions of surfactants, a larger surfactant length (for fixed X) implies a larger period D of the structure. The width of the surfactant-rich regions of the ordered structures increases due to both an increase of surfactant volume fraction and a decrease of the degree of association resulting in an increase of the period as a whole.

3.4. Reappearing phases

Reappearing phases is a characteristic phenomenon which can take place in polymer systems with hydrogen bonding. It refers to the situation where the homogeneous state is unstable for higher temperatures but becomes stable again as the temperature decreases or increases (e.g. closed loop region of macrophase separation). It results from the specific temperature dependence of hydrogen bond formation. According to the theoretical analysis, it can happen only for a special class of polymer/surfactant mixtures, namely those mixtures with strong hydrogen bonding characterized by the average fraction of hb, X_{hb}, rapidly changing with temperature. In terms of the energetic gain E and the entropic loss S accompanying hb formation, it is a polymer system with a large value of E, and not too small value of S. Thus, for elevated temperatures the entropy loss is large which prevents hydrogen bonding. Whereas for temperatures below some 'critical temperature' hydrogen bonding occurs very extensively. Hence, X_{hb} increases rapidly in a

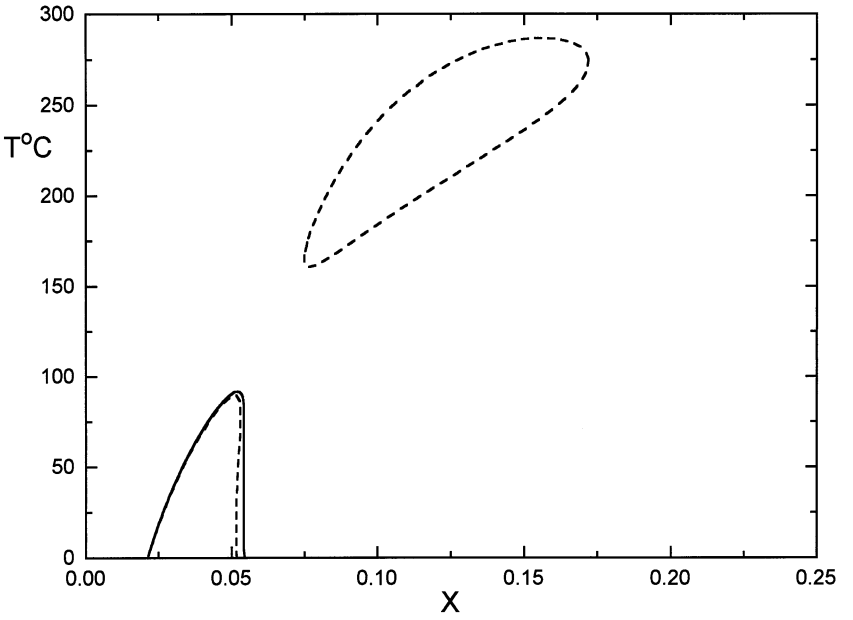

Fig. 9. Spinodal curves for macro- (dashed curve) and microphase (solid curve) separation for the polymer–surfactant mixture ($N_p = 10^3$, $N_{s=}20$, $E = 1000$ K, $S = 2.087$, $\Theta = 82$ K).

relatively narrow temperature range below the critical 'temperature'.

Calculated spinodal curves for micro- and macrophase separation for such a polymer/surfactant system are presented in Fig. 9. Besides the region of instability similar to that of Fig. 4 at low temperatures, there is also an instability region with respect to macrophase separation for elevated temperatures. These two regions of instability are separated by a stable homogeneous phase at an intermediate temperature range. The complete phase diagram is presented in Fig. 10. For high temperatures ($T > 285$°C), the homogeneous state of polymer system is stable. A decrease in temperature results in an increase of the segregation tendency and the polymer/surfactant mixture separates into two homogeneous phases, one polymer-rich and one surfactant-rich ($285 \leq T \leq 160$). For lower temperatures ($160 \leq T \leq 92$) the incompatibility of the components increases, however, simultaneously the average fraction of hb per chain X_{hb} substantially increases. Comb copolymer-like chains with surfactants playing the role of side chains become compatible with a 'solvent' of free surfactants. As a result the homogeneous state is stable again. For even lower temperatures ($T \leq 92$), the polymer–surfactant system separates again into a homogeneous and an ordered (hexagonal for the present case) phase. The region of stable ordered structure is located in the region of low surfactant fraction as for the case of Fig. 5. But note that $X = 0.05$ corresponds to equal volume fractions.

The phase diagram of Fig. 10. can be compared with experimental data obtained for the polymer mixture of P4VP-$MSA_{1.0}$-$PDP_{1.0}$ [16]. In this system, the stable homogeneous state above 200°C becomes unstable with respect to macrophase separation in the temperature range 175–200°C. For lower temperatures (100–175°C), the homogeneous state becomes stable again. Finally, for temperatures below 100°C the system is in a microphase separated state with a lamellar morphology. Hence, the order of phase transformations is very similar to that of the theoretical model, especially for $X \simeq 0.07$. Of course, it is unrealistic to expect a precise quantitative coincidence in the theoretical and the experimental results since as discussed above, the theoretical model does not take into account some specific features of the experimental system.

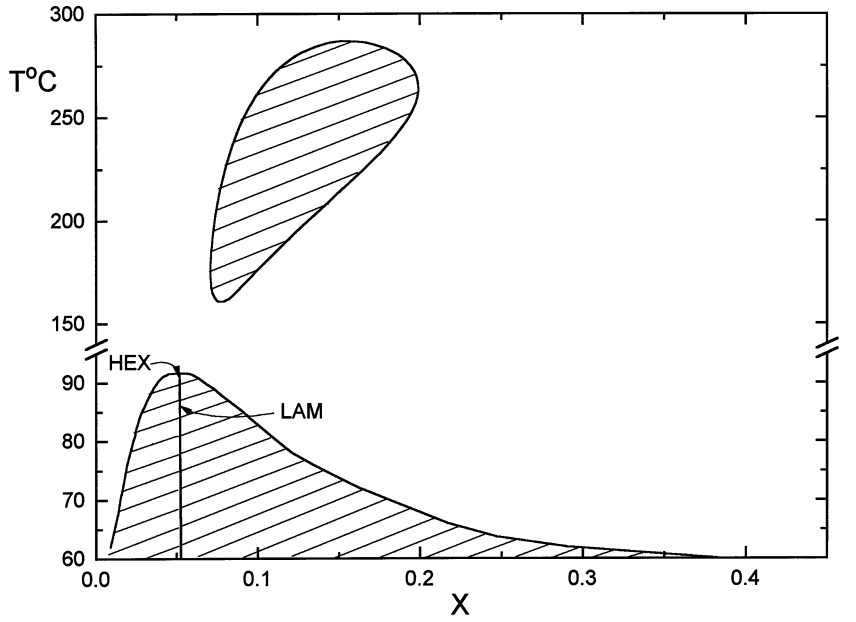

Fig. 10. Phase diagram for the polymer–surfactant mixture ($N_p = 10^3$, $N_s = 20$, $E = 1000$ K, $S = 2.087$, $\Theta = 82$ K). Diagram contains the regions of stability of hexagonal (HEX) and lamellar (LAM) ordered phases as well as regions of macrophase separation (shaded areas).

The presence of charges in P4VP-MSA-PDP mixtures might influence the phase behaviour as well, due to possible cooperativeness of hydrogen bond formation for this system, which is in contrast with the basic assumptions of the theoretical model. Nevertheless, the qualitative agreement between the theoretical predictions and the real behavior of the polymer system is evident. This means, that the phenomenon of reappearing phases has a common background resulting from a temperature dependence of the hydrogen bond formation, valid for both charged and uncharged polymer systems.

4. Conclusion

The model proposed offers a description of hb formation and phase behavior for polymer/surfactant systems with different composition and different strength of hydrogen bonding. The phase diagrams obtained in the weak segregation approximation could be compared with available experimental data, but only in a semi-quantitative manner. A one-to-one correspondence between the theoretical model and the experimental systems based on P4VP and alkyl phenols is not possible due to the large difference in hard-core volume between the units of the polar 'backbone' (i.e. vinylpyridine + phenol) and the units of the alkyl side chains (i.e. CH_2).

The phase diagram for the model with strong hydrogen bonding shows that stable ordered structures can only be formed for comparable volume fractions of polymer and surfactant, which corresponds to small values of X for the theoretical model (i.e. $X \leq 0.1$). Macrophase separation into a homogeneous and an ordered (hexagonal or lamellar) phase takes place for a wide composition range. Experimentally, P4VP-PDP_X seems to exhibit only a single lamellar phase [9,11,13–16]. However, the ubiquitous presence of macrophase separation in the theoretical modeling clearly indicates the need for a systematic study of the possibility of macrophase separation between an ordered and a homogeneous phase. Large time effects may also play a role.

According to the experimental observations [11,13,16] and the results of the theoretical model, the period of the ordered structure D decreases as the surfactant fraction increases until stoichiometric composition (i.e. $X=1$). It is important to note, however, that only the experimental data related to the ODT can be compared with the theoretical results because of the limitations of the RPA approach.

An increase of the surfactant length results in an increase of the order–disorder transition temperature, as follows from both theoretical and experimental results [16]. The reason for this phenomenon is that a decrease of the polymer volume fraction for longer surfactants results in a decrease of the average degree of complexation and therefore makes the polymer system less stable with respect to micro- (macro-) phase separation. The period of the ordered structures (corresponding to ODT temperature) increases with an increase of the surfactant length in a wide composition range.

The specific temperature dependence of hydrogen bonding can result in the characteristic phenomenon of reappearing phases. The reason is the abrupt decrease of the average fraction of hb per chain X_{hb} with increasing temperature, resulting in a destabilization of the homogeneous state. This phenomenon has been observed experimentally for P4VP-$MSA_{1.0}$-$PDP_{1.0}$ [16].

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